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Signed this 31st day of May 2007



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For and on behalf of RWS Group Ltd

FEDERAL REPUBLIC OF GERMANY

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Title: (Diene)bis(aquo)rhodium(I) complexes, process for preparing them
and their use

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Letang

New German patent application
Umicore AG & Co. KG
U.Z. G5466 DE

5 **(Diene)bis(aquo)rhodium(I) complexes, process for
 preparing them and their use**

10 The present invention relates to (diene)bis(aquo)-
rhodium(I) complexes, a process for preparing them and
their use in catalytic reactions and for producing
heterogeneous catalysts.

15 More than 80% of industrially produced chemicals are
produced with the aid of catalytic processes. Catalytic
processes are generally more economical and more
environmentally friendly than corresponding
stoichiometric organic reactions.

20 In homogeneously catalysed processes using metal
compounds as homogeneous catalysts, the broad use
spectrum of the catalysts requires a large range of
possible ligand systems. Thus, in order to achieve high
yields and selectivities in homogeneously catalyzed
25 processes, it is necessary to make an optimal choice
from a variety of ligand systems, which consequently
also increases the need for universally usable
precursor metal compounds. The need for continually
improving the catalyst systems and processes for
producing them is thus clear.

30

The majority of the homogeneously catalyzed processes
and reactions described in the prior art concern
symmetric and asymmetric hydrogenation reactions of
C-C, C-O, C-S and C-N bonds. Precursor metal compounds
35 for such reactions which are of great industrial
interest are, for example, provided by monomeric and
polymeric ruthenium(II) complexes or mononuclear or
binuclear rhodium(I)-olefin complexes.

Rhodium(I)-olefin complexes are widely used, for example, as catalysts in symmetric and asymmetric hydrogenation reactions, in hydroformylations, hydrosilylations and coupling reactions. Numerous
5 rhodium(I)-olefin complexes are known in the art, as described, for example, in Houben-Weyl "Methoden der organischen Chemie" (4th Edition, Vol. XIII/9b, "Metallorganische Verbindungen"). All these known complexes have olefinic units which coordinate to the
10 rhodium and stabilize the metal in its respective oxidation state.

Typical olefins present in such complexes are, for example, 1,5-cyclooctadiene (COD), 1,3-cyclooctadiene,
15 norbornadiene (NBD), cyclooctatriene, butadiene, various alkylated and/or substituted butadiene derivatives and ethylene. One of the most frequently used dienes is 1,5-cyclooctadiene (COD).

20 Since the rhodium is always in the formal oxidation state +1 in the abovementioned complexes, anionic counterions are always necessarily present. Among these anions, a distinction can be made between those which are coordinated to the rhodium, for example halide,
25 silyl or alkoxy anions, acetates or sulphonates, and those which are present without coordinating, for example PF_6^- , BF_4^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$, and other borate derivatives and also various sulphonates, nitrates and perchlorates.

30 Apart from purely olefinically coordinated complexes, i.e. complexes in which only olefins or the counterion coordinate to rhodium, mixed complexes in which not only the olefin but also further ligands coordinate to
35 rhodium are also known. The ligands here can be, for example, phosphine or phosphite ligands, amines, arsanes or coordinating organic solvents.

Various mixed complexes of this type, e.g. having

methanol, ethanol, acetone or acetonitrile as organic solvents of which two molecules are coordinated in addition to a diene, usually COD or NBD, or a phosphine to the rhodium, have been described in the prior art
5 (see, for example, Osborn et al., Angew. Chemie 99 (1987) 1208-1209). Such complexes described in the prior art have a composition corresponding to one of the general formulae $[\text{Rh}(\text{diene})\text{L}_2]\text{X}$ or $[\text{Rh}(\text{chiral phosphine ligand})(\text{L})_2]\text{X}$, where diene is 1,5-cyclo-
10 octadiene (COD) or norbornadiene (NBD), L is acetone, acetonitrile, methanol or ethanol and X is an anion selected from among BF_4^- and CF_3SO_3^- .

Some of the compounds described in the prior art have
15 been postulated as intermediates, i.e. *in situ* preparations (as in, for example, Schrock et al, J. Am. Chem. Soc. 93 (1971) 2397-2407 for L = methanol or acetone), or as precursors of catalysts in hydrogenation reactions or identified in solution by
20 means of NMR spectroscopy. Isolation and separate characterization of these complexes has not been able to be achieved in the past because of their presumably low stability in the case of, for example, L = acetone.

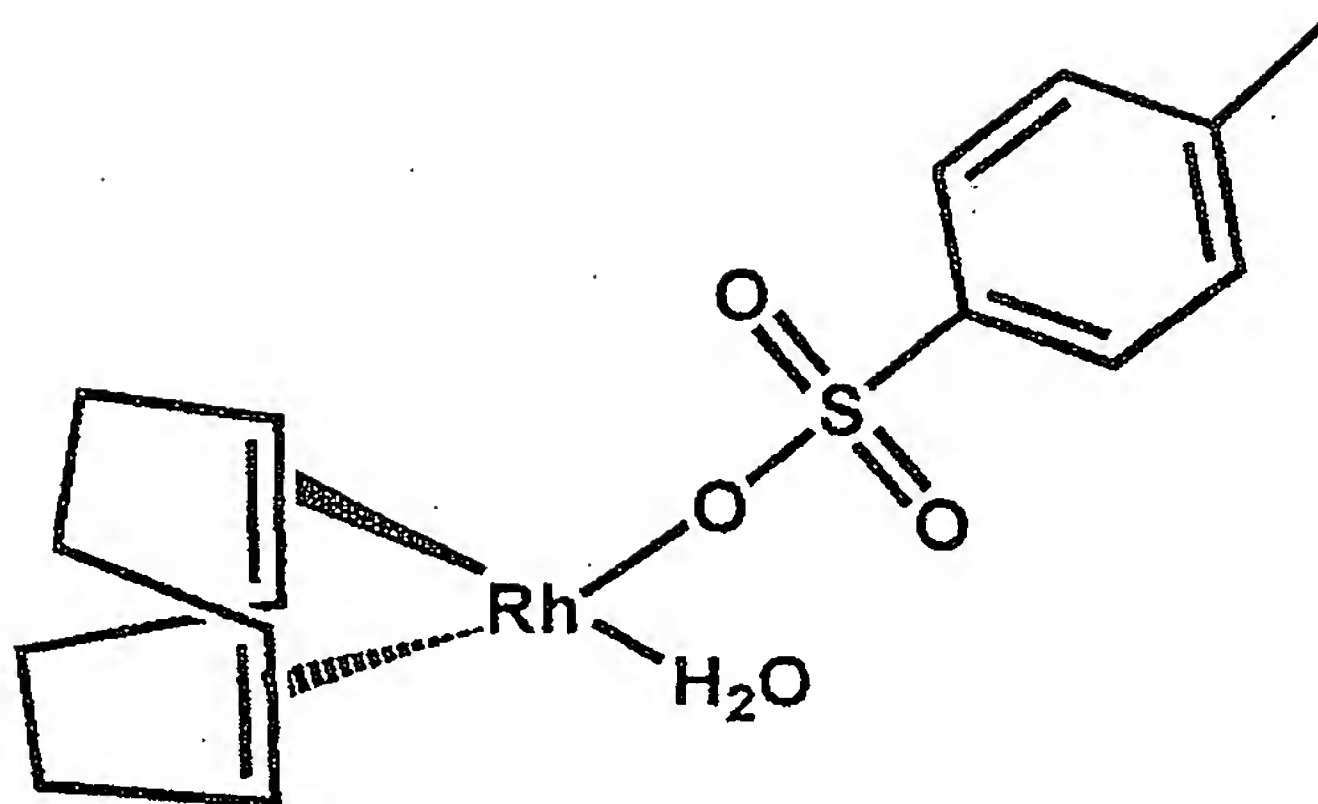
25 Bergbreiter et al. (Tetrahedron Letters (1997), 38(21), 3703-3706, and Chemical Industries (Dekker) (1998), 75 (Catalysis of Organic Reactions), 403-414) describe the use of $[\text{Rh}(\text{COD})]\text{CF}_3\text{SO}_3$. However, the structure and the method of preparing the compound remain undefined and
30 are not revealed by the prior art.

Harry et al. (Inorganica Chimica Acta 97 (1985) 143-150) disclose the preparation and use of $[\text{Rh}(\text{COD})]\text{CF}_3\text{SO}_3$. The structure of the compound described
35 remains unelucidated. The catalytic data obtained are not in agreement with the structure as proposed above. Isolation of a complex of the formula $[\text{Rh}(\text{COD})(\text{L})_2]\text{CF}_3\text{SO}_3$ where L = coordinating solvent as a solid is not described; the compounds are merely

postulated in solution.

In Chem. Ber. 128 (1995) 911-917, Kölle et al. describe the preparation of various olefin-aquo complexes of rhodium(I). Specifically, the preparation, isolation and use of $[\text{Rh}(\text{COD})(\text{H}_2\text{O})(\text{p-toluenesulphonate})]$ is disclosed. In addition, Kölle et al. describe the *in-situ* preparation of a series of complexes of the general formula $[\text{Rh}(\text{diene})\text{L}_2]\text{X}$, where diene is 1,5-cyclooctadiene (COD) or norbornadiene (NBD), L is acetone or water and X is an anion selected from among $\text{p-CH}_3(\text{C}_6\text{H}_4)\text{SO}_3^-$ (tosylate, OTs^-), CF_3SO_3^- and BF_4^- . The preparation of these compounds is carried out using solid silver salts and in solvent mixtures of water and ethanol which are not described in more detail. Some of the compounds mentioned have been postulated as intermediates on the basis of NMR-spectroscopic studies, but only in solution. However, experimental confirmation of the bis-aquo complexes was not able to be carried out successfully. It was merely possible to prepare corresponding complexes with monoolefins, e.g. ethylene, or open-chain 1,3-dienes, e.g. isoprene.

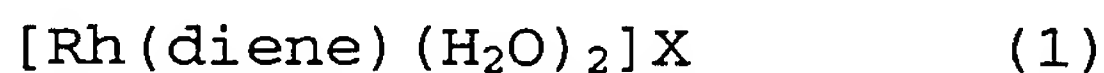
According to Kölle et al., attempts to isolate a complex of the formula $[\text{Rh}(\text{COD})(\text{H}_2\text{O})_2]\text{X}$ failed and led, in the case of OTs^- as anion X, to the complex $[\text{Rh}(\text{COD})(\text{H}_2\text{O})\text{OTs}]$, i.e. a mono-aquo complex. The structure of this complex was able to be confirmed by means of X-ray structure analysis, and the structure determined is shown in the following figure:



It is an object of the present invention to provide novel (diene)bis(aquo)rhodium(I) complexes.

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The object of the invention is achieved by a process according to the invention for preparing (diene)bis(aquo)rhodium(I) complexes, which process comprises reacting rhodium(I)-olefin compounds with
10 silver salts in an aqueous solvent mixture, characterized in that the silver salt is not added as a solid to the reaction mixture but is prepared and added in solution. The invention further provides (diene)bis(aquo)rhodium(I) complexes of the general
15 formula (1):



where diene is a cyclic diene and X is a
20 noncoordinating anion. The present invention also relates to the use of the (diene)bis(aquo)rhodium(I) complexes of the invention in catalytic reactions.

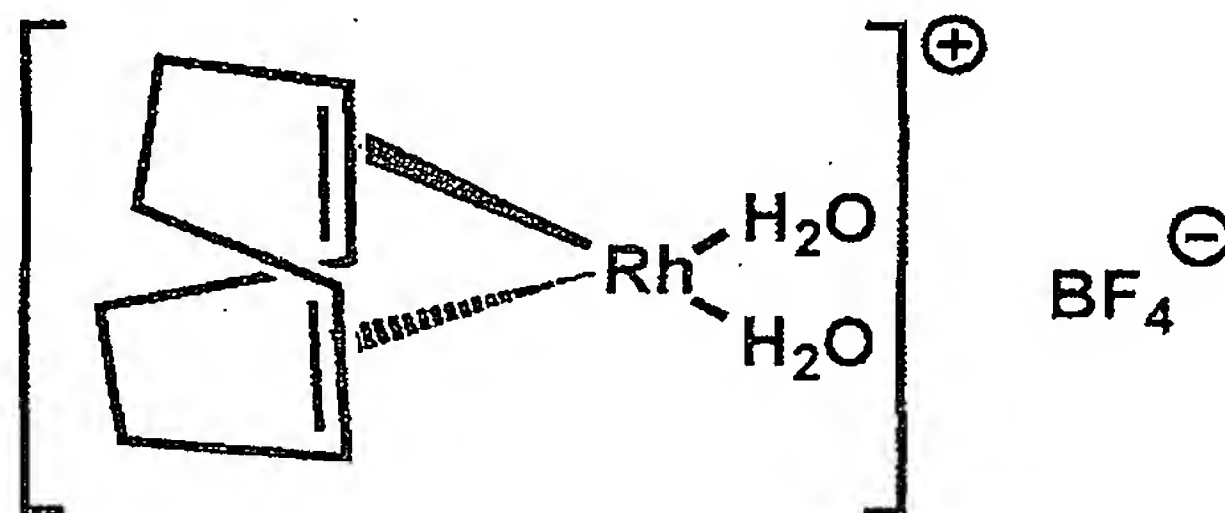
As cyclic diene in the general formula (1), it is
25 possible to use any cyclic diene which is able to coordinate to a central metal atom in complexes. According to the invention, cyclic dienes used can be, for example, cyclic hydrocarbons having from 5 to 12 carbon atoms and two C-C double bonds in the ring.
30 Preference is given, according to the invention, to cyclic dienes in which the two C-C double bonds are not

conjugated. As examples of cyclic dienes according to the invention, mention may be made of 1,4-cyclohexadiene, 1,4-cycloheptadiene, 1,5-cyclooctadiene (COD), norbornadiene (NBD) and various camphene derivatives.

- 5 Particularly preferred cyclic dienes for the purposes of the invention are 1,5-cyclooctadiene (COD) and norbornadiene (NBD). Particular preference is given to 1,5-cyclooctadiene (COD).
- 10 The radical X in formula (1) is a noncoordinating anion. According to the invention, X can be any anion which is known in the art to be able to be present in a noncoordinating fashion in metal complexes, in particular in rhodium compounds, particularly
- 15 preferably rhodium(I) compounds. As examples of noncoordinating anions according to the present invention, mention may be made of CF_3SO_3^- , BF_4^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$, $\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4^-$, $\text{B}(\text{C}_6\text{F}_5)_4^-$, PF_6^- , SbF_6^- and ClO_4^- . Particular preference is given to tetrafluoroborate
- 20 (BF_4^-) and trifluoromethylsulphonate (triflate, CF_3SO_3^-).

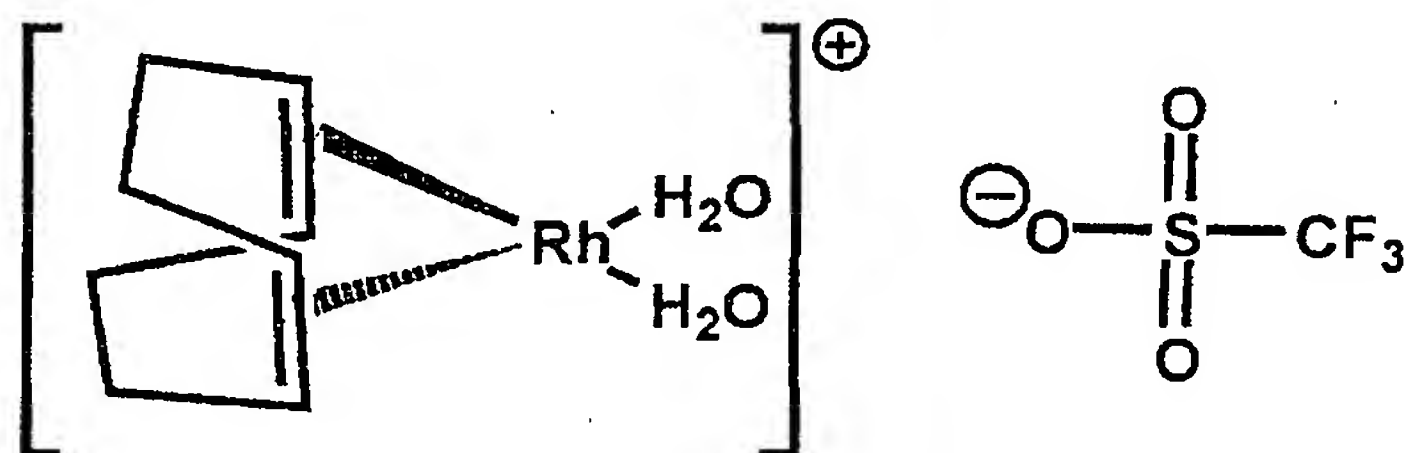
In a particularly preferred embodiment of the present invention, the diene in formula (1) is 1,5-cyclooctadiene (COD) and the anion is BF_4^- . This complex of the

25 formula $[\text{Rh}(\text{COD})(\text{H}_2\text{O})_2]\text{BF}_4$ is referred to as (1,5-cyclooctadiene)bis(aquo)rhodium(I) tetrafluoroborate and has the structure below:



In a further particularly preferred embodiment of the present invention, the diene in formula (1) is 1,5-

cyclooctadiene (COD) and the anion is CF_3SO_3^- . This complex of the formula $[\text{Rh}(\text{COD})(\text{H}_2\text{O})_2]\text{CF}_3\text{SO}_3$ is referred to as (1,5-cyclooctadiene)bis(aquo)rhodium(I) trifluoromethylsulphonate or triflate and has the structure below:



The (diene)bis(aquo)rhodium(I) complexes of the invention described can be provided both in solution or suspension in any solvent, for example halogen-containing solvents, water, alcohols and ethers, preferably as a solution in water, alcohols such as methanol or ethanol, ethers such as tetrahydrofuran, dioxane and diethyl ether or acetone or in mixtures thereof, and also as isolated substances. The (diene)bis(aquo)rhodium(I) complexes of the present invention are preferably provided as solids.

A method known in the art for introducing anionic ligands into metal complexes is the transmetallation reaction. It is based on the principle of reacting a precursor compound which is made up of the cation of the desired complex and a replaceable anion with a suitable metal salt of the anion to be introduced into the complex. Silver salts have in the past been found to be particularly useful metal salts for introducing various anions into metal complexes, with the appropriate silver salt generally being added as a solid to the reaction mixture.

The process of the present invention for preparing the (diene)bis(aquo)rhodium(I) complexes of the invention

is characterized in that the appropriate silver salt which serves as transmetallating reagent is not added as a solid to the reaction mixture but is prepared and added in solution. To prepare a silver salt solution according to the present invention, preference is given to reacting a silver-containing starting compound, particularly preferably a basic silver salt such as silver oxide (Ag_2O), with a suitable acid, preferably in a suitable solvent, with elimination of water in the case of Ag_2O as starting compound so as to give a solution of the desired silver salt. As suitable acid, the acid corresponding to the noncoordinating anion to be introduced into the (diene)bis(aquo)rhodium(I) complex, e.g. trifluoromethanesulphonic acid for preparing a solution of AgCF_3SO_3 , is chosen here.

The preparation of the silver salt solution by reacting Ag_2O with the appropriate acid is preferably carried out in an aqueous medium. For the purposes of the invention, an aqueous medium encompasses not only water as sole solvent but all solvent mixtures in which water is the main component of the mixture and is mixed with one or more water-miscible solvents. Examples of such water-miscible solvents are alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol, ethers such as tetrahydrofuran or dioxane and acetone. An aqueous medium according to the invention can also comprise water and a water-miscible solvent together with at least one further solvent which is not miscible with water, as long as the solvent mixture forms a homogeneous phase. Examples of such solvents according to the invention which are not miscible with water are diethyl ether and methyl tert-butyl ether. The use of water as solvent for preparing the silver salt solution according to the invention is particularly preferred.

The respective acid is preferably used in an excess over the silver oxide in the preparation of the silver

salt solution. This excess of acid can be up to 0.5 molar equivalent, preferably from 0.01 to 0.15 molar equivalent. The particularly preferred excess of acid over the silver oxide can depend in the individual case on the type of acid used; in particular, the silver oxide should have dissolved completely after the addition is complete. In the preparation of an AgBF_4 solution according to the process of the invention, the acid HBF_4 is particularly preferably used in an excess of about 0.03 molar equivalent based on the silver oxide, and in the preparation of an AgCF_3SO_3 solution according to the invention, the particularly preferred excess of $\text{CF}_3\text{SO}_3\text{H}$ is about 0.07 molar equivalent.

As rhodium(I)-olefin compounds which can be used as starting materials in the process of the invention, it is in principle possible to use all rhodium(I)-olefin compounds which can react in a transmetallation reaction with the silver salt solution according to the invention to effect transmetallation and form the (diene)bis(aquo)rhodium(I) complexes of the invention. As preferred rhodium(I)-olefin compounds according to the present invention, it is possible to use complexes of the general formula $[\text{Rh}(\text{diene})\text{Y}]_2$, where Y is Cl, Br or I and diene is as defined above. A particularly preferred rhodium(I)-olefin compound which can serve as starting compound for the transmetallation reaction is the dimeric rhodium complex $[\text{Rh}(\text{COD})\text{Cl}]_2$.

As aqueous solvent mixture in which the reaction of the rhodium(I)-olefin compound with the silver salt can be carried out according to the process of the invention, it is possible to use all solvent mixtures which comprise water as a constituent. Further constituents of a solvent mixture according to the invention can be any water-miscible solvents. The aqueous solvent mixture preferably comprises water together with up to 10% by volume of at least one alcoholic solvent. As preferred alcoholic solvents, it is possible to use, in

particular, methanol, ethanol, n-propanol, isobutanol, n-butanol and tert-butanol according to the invention.

5 In the process of the invention, the reaction of the rhodium(I)-olefin compound with the appropriate silver salt in the aqueous solvent mixture is preferably carried out by adding the previously prepared silver salt solution to a solution or suspension of the rhodium(I)-olefin compound in an aqueous solvent
10 mixture according to the invention. The addition of the silver salt solution to the solution or suspension of the rhodium(I)-olefin compound in the aqueous solvent mixture can be effected either by immediate addition of the total amount of silver salt solution or by slow
15 dropwise addition of the silver salt solution over a relatively long period of time, for example up to one hour.

After addition of the total amount of silver salt
20 solution, the reaction mixture is stirred for a suitable period of time, with a silver salt formed as by-product of the transmetallation reaction precipitating as solid. To isolate the desired (diene)bis(aquo)rhodium(I) complex, the precipitated
25 solid is subsequently filtered off and washed as often as necessary with a suitable solvent, preferably water. The solvent can be removed from the filtrate obtained in a manner known in the art, for example by evaporation on a rotary evaporator, in order to isolate
30 the desired (diene)bis(aquo)rhodium(I) complex as a solid.

Both in the preparation of the silver salt solution and in the reaction with the rhodium(I)-olefin compound,
35 the working temperature should, according to the present invention, be selected so that the resulting (diene)bis(aquo)rhodium(I) complexes of the present invention do not decompose. For this reason, a temperature of 40°C should not be exceeded as working

temperature while the (diene)bis(aquo)rhodium(I) complexes of the invention are present in solution. The reactions are particularly preferably carried out at room temperature.

5

The (diene)bis(aquo)rhodium(I) complexes of the invention can be used in catalytic reactions, i.e. in both homogeneous and heterogeneous catalysis. In particular, the (diene)bis(aquo)rhodium(I) complexes of
10 the present invention are suitable for use in asymmetric and symmetric catalytic hydrogenations of double bonds, for example C-C, C-O, C-N or N-N double bonds. Another field of application comprises catalytic hydroformylation reactions and hydrosilylations.

15

Furthermore, the (diene)bis(aquo)rhodium(I) complexes of the invention can be used as precursors for other catalytically active species. The (diene)bis(aquo)-rhodium(I) complexes of the invention can in this case
20 be used for preparing chirally unselective, diastereoselective or enantioselective catalytically active species. To generate such catalytically active species, the (diene)bis(aquo)rhodium(I) complexes of the invention can be reacted with various achiral and
25 chiral ligands, for example triphenylphosphine, ferrocenylphosphines, alkylphosphines or chiral phosphine ligands, with ligand replacement taking place.

30 The (diene)bis(aquo)rhodium(I) complexes of the invention can also be used for producing heterogeneous catalysts, in which case all processes known in the art for making soluble organometallic complexes heterogeneous are possible for producing these. In a
35 particularly preferred embodiment, a (diene)bis(aquo)-rhodium(I) complex according to the invention can be used as supported or immobilized noble metal catalyst.

Examples

Example 1: Preparation of $[\text{Rh}(\text{COD})(\text{H}_2\text{O})_2]\text{BF}_4$

- 5 4.63 g of aqueous HBF_4 solution (about 50% strength, 26.36 mmol of HBF_4 , excess based on Ag_2O : 0.03 molar equivalent) and 10 g of distilled water are weighed into a glass beaker. In addition, 2.96 g of Ag_2O (12.77 mmol) are weighed out on a paper boat. The Ag_2O is carefully added by means of the paper boat to the aqueous HBF_4 solution over a period of one minute, after which the mixture is stirred vigorously. An AgBF_4 solution is obtained.
- 15 6.0 g of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (41% of Rh, 2.46 g of Rh, 23.9 mmol) are weighed into a second glass beaker and suspended in 10 g of distilled water and 0.3 g of ethanol (corresponding to about 1.5% by volume of the resulting total solution) with stirring (RCT Basic, setting 4-5) for 7 minutes. All of the AgBF_4 solution prepared in the first step is poured into the suspension obtained while stirring, whereupon a precipitate is formed. The resulting light-yellow suspension is stirred for about 30 minutes. The precipitate is subsequently filtered off and washed twice with about 5 ml of distilled water. The solution obtained is finally evaporated at 40°C under reduced pressure on a rotary evaporator. 7.96 g of the title product are isolated (30.3% of Rh, 2.41 g of Rh, 23.4 mmol, yield: 98% based on Rh).

Analysis: $\text{C}_8\text{H}_{16}\text{O}_2\text{BF}_4\text{Rh}$, $M = 333.9233$ g/mol.

^1H -NMR (CDCl_3 , 500 MHz): δ (ppm) = 1.57 (s, 4 H), 5.46-5.57 (m, 8 H).

^1H -NMR (d-dioxane, 500 MHz): δ (ppm) = 1.73 (dt, $J = 7.2$ Hz, $J = 8.5$ Hz, 4 H), 2.50-2.53 (m, 4 H), 4.05 (m, 4 H).

^1H -NMR (MeOD, 500 MHz): δ (ppm) = 1.72 (dt, J = 6.9 Hz, J = 8.5 Hz, 4 H), 2.51-2.54 (m, 4 H), 4.07 (m, 4 H).

5 IR (KBr, cm^{-1}): 3436 (vs), 2939 (m), 2876 (m), 2803 (m), 1639 (m), 1467 (w), 1429 (m), 1325 (w), 1299 (m), 1061 (vs), 958 (m), 794 (m), 521 (m).

Rh% (measured by ICP = inductively coupled plasma):

% theor.: 30.82

% pract.: 30.30

10 Elemental analysis:

% C theor. 28.77

% C pract. 28.56

% H theor. 4.83

% H pract. 4.98

15

The structure of the complex was able to be confirmed by X-ray crystal structure analysis.

Example 2: Preparation of $[\text{Rh}(\text{COD})(\text{H}_2\text{O})_2]\text{CF}_3\text{SO}_3$

20

4.92 g of Ag_2O (21.26 mmol) and 10 g of distilled water are weighed into a glass beaker and 4.1 ml of trifluoromethanesulphonic acid (about 98% strength, 45.40 mmol, excess based on Ag_2O : 0.07 molar equivalent) are carefully added. While stirring vigorously, a further 10 g of distilled water are added. An AgCF_3SO_3 solution is obtained.

25

9.94 g of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (41% of Rh, 4.08 g of Rh, 39.6 mmol) are weighed into a second glass beaker and suspended in 10 g of distilled water and 0.82 ml of ethanol (corresponding to about 0.5% by volume of the resulting total mixture) and 12.7 ml of methanol (corresponding to about 9.5% by volume of the resulting total mixture) with stirring (RCT Basic, setting 4-5) for seven minutes. All of the AgCF_3SO_3 solution prepared

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35

in the first step is added dropwise to the suspension
obtained over a period of 30 minutes while stirring and
the AgCF_3SO_3 solution is rinsed in using two portions of
5 g of distilled water. A precipitate is formed. The
5 resulting light-yellow suspension is stirred for about
30 minutes. The precipitate is subsequently filtered
off and washed six times with about 5 ml of distilled
water. The solution obtained is finally evaporated at
40°C under reduced pressure on a rotary evaporator.
10 15.3 g of the title product are isolated as an orange
solid (25.3% of Rh, 3.87 g of Rh, 37.60 mmol, yield:
95% based on Rh).

Analysis: $\text{C}_9\text{H}_{16}\text{O}_5\text{SF}_3\text{Rh}$, $M = 396.1879$ g/mol.

15 ^1H -NMR (CDCl_3 , 500 MHz): δ (ppm) = 1.25 (s, 4 H), 2.50-
2.53 (m, 4 H), 4.09 (m, 4 H).

^1H -NMR (d-dioxane, 500 MHz): δ (ppm) = 1.66 (dt, $J =$
20 7.2 Hz, $J = 8.5$ Hz, 4 H), 2.45-2.47 (m, 4 H), 4.02 (m,
4 H).

^1H -NMR (MeOD, 500 MHz): δ (ppm) = 1.63 (dt, $J = 6.9$ Hz,
 $J = 8.5$ Hz, 4 H), 2.38-2.40 (m, 4 H), 3.93 (m, 4 H).

25 ^{13}C -NMR (MeOD, 125 MHz): δ (ppm) = 31.57 (d, 4 C), 78.81
(d, $J = 15.2$ Hz, 4 C), 121.61 (q, $J = 318.5$ Hz).

IR (KBr, cm^{-1}): 3415 (vs), 2998 (s), 2924 (s), 2879 (s),
30 1646 (m), 1433 (w), 1254 (vs), 1178 (vs), 1032 (vs),
969 (m), 643 (s), 582 (m), 518 (m).

Rh% (measured by ICP = inductively
coupled plasma):

% theor.: 25.97

% pract.: 25.30

Elemental analysis:

35 % C theor. 27.28

% C pract. 26.95

% H theor.	4.07
% H pract.	4.3
% S theor.	8.09
% S pract.	8.33

5

The structure of the complex was able to be confirmed by X-ray crystal structure analysis.

New German patent application

Umicore AG & Co. KG

G5466 DE

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CLAIMS

1. (Diene)bis(aquo)rhodium(I) complex of the general formula (1):

10



where diene is a cyclic diene and X is a noncoordinating anion.

15

2. (Diene)bis(aquo)rhodium(I) complex according to Claim 1, wherein diene is 1,5-cyclooctadiene (COD) or norbornadiene (NBD).

20

3. (Diene)bis(aquo)rhodium(I) complex according to Claim 1 or 2, wherein X is a noncoordinating anion selected from among BF_4^- and CF_3SO_3^- .

25

4. (Diene)bis(aquo)rhodium(I) complex according to any of Claims 1 to 3 which is (1,5-cyclooctadiene)bis(aquo)rhodium(I) tetrafluoroborate.

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5. (Diene)bis(aquo)rhodium(I) complex according to any of Claims 1 to 3 which is (1,5-cyclooctadiene)bis(aquo)rhodium(I) trifluoromethylsulphonate.

6. (Diene)bis(aquo)rhodium(I) complex according to any of Claims 1 to 5 which is present as a solid.

35

7. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to any of Claims 1 to 6, which process comprises reacting a rhodium(I)-olefin compound with silver salts in an aqueous solvent mixture, characterized in that the silver salt is not added as a

solid to the reaction mixture but is prepared and added in solution.

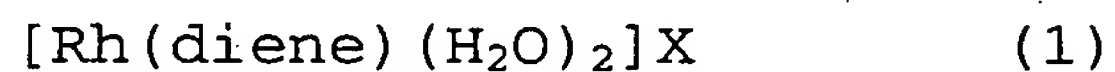
- 5 8. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to Claim 7, wherein the preparation of the silver salt in solution is carried out by reacting silver oxide (Ag_2O) with the acid corresponding to the noncoordinating anion of the (diene)bis(aquo)rhodium(I) complex.
- 10 9. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to Claim 8, wherein the acid is used in an excess of up to 0.5 molar equivalent based on the silver oxide.
- 15 10. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to any of Claims 7 to 9, wherein the preparation of the silver salt is carried out in an aqueous medium.
- 20 11. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to any of Claims 7 to 10, wherein the rhodium(I)-olefin compound is $[\text{Rh}(\text{COD})\text{Cl}]_2$.
- 25 12. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to any of Claims 7 to 11, wherein the aqueous solvent mixture comprises water together with up to 10% by volume of at least one alcoholic solvent.
- 30 13. Process for preparing a (diene)bis(aquo)rhodium(I) complex according to Claim 12, wherein the alcoholic solvent is selected from among methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol.
- 35 14. Use of a (diene)bis(aquo)rhodium(I) complex according to any of Claims 1 to 6 in catalytic reactions.
15. Use of a (diene)bis(aquo)rhodium(I) complex

according to any of Claims 1 to 6 for producing heterogeneous catalysts.

New German patent application
Umicore AG & Co. KG
G5466 DE

ABSTRACT

(Diene)bis(aquo)rhodium(I) complex of the general formula (1):



where diene is a cyclic diene and X is a noncoordinating anion, a process for preparing it and its use.